Preparation and Characterization of Barium Strontium Titanate Ceramics by Gel-Combustion Technique.

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Bachelor of Technology

By

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(Shilpi Agarwal)

National Institute of Technology Rourkela

CERTIFICATE

This is to certify that the thesis entitled, *"Preparation and Characterization of Barium Strontium Titanate Ceramics by Gel Combustion Technique"* submitted by Ms. **Shilpi Agarwal** in partial fulfillments for the requirements for the award of **Bachelor of Technology** degree in **Ceramic Engineering** at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

Date: 13-05-2013

Prof Arun Chowdhury
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ABSTRACT

Barium Strontium Titanate ($Ba_{0.8}Sr_{0.2}TiO_3$) has been prepared and characterized in this present study. BST phase pure powder has been prepared following combustion synthesis technique and the sol-gel route. Citric acid and ethylene glycol have been used as a fuel in this combustion process. Use of ammonia solution to maintain the pH 7 is a must requirement. EDTA is the chelating agent with helps in the complex formation before gel formation in the combustion process. Preparation of titanium oxy-nitrate is the integral part of all the synthesis procedure. Bulk ceramic samples are prepared following the combustion technique while thin films are prepared by sol gel route and dip coating technique. X-ray diffraction of the bulk and coated substrates are done. The densification behavior and densification kinetics of the BST powder has also been studied. Powder morphology and microstructure of sintered BST bulk samples and the thick films was determined. Dielectric behavior of BST samples has also been studied as a function of frequency at room temperature.

Chapter 1

INTRODUCTION

INTRODUCTION

Ferroelectric materials have field dependent dielectric permittivity. When an electric field is applied to a dielectric material, polarization of charges occurs. Most ferroelectric materials are found to have perovskite structure (ABO_3). 'A' atoms are divalent, 'B' atoms are placed body Centre and have +4 charge on them. 'O' atoms occupies the face centre of the cubic crystal lattice. Ferroelectric with perovskite structure are put to variety of applications such as high permittivity capacitors, tunable microwave devices, pyroelectric sensors and piezoelectric transducers etc. ferroelectric tends to become paraelectric beyond a transition temperature called curie temperature. At Curie temperature the ferroelectric material undergo a structural change from ferroelectric to paraelectric attaining highest dielectric constant. A strong hysteresis behavior is observed in case of ferroelectric and hence it makes ferroelectric materials applicable for non-volatile memory applications.

Perovskites have high dielectric properties over a wide temperature and frequency range. There is a growing interest in ferroelectric materials for memory applications as Ferroelectric Dynamic Random Access Memory (FDRAMs), where the direction of spontaneous polarization is used to store information digitally in replacement to SiO_2/Si_3N_4 dielectrics as the storage mediums in conventional DRAMs.

$Ba_{1-x}Sr_xTiO_3$ (BST) is known to adopt ABO_3 type structure in a continuous solid solution of $BaTiO_3$ and $SrTiO_3$ over the whole concentration range. $SrTiO_3$ is usually added as a shifter in order to move the Curie point Tc to lower temperature. The non-linearity of its dielectric properties with respect to applied DC voltage makes it attractive for tunable microwave devices such filters, varactors, delay lines and phase shifters. Over the last decade, there has been strong interest in the development of BST tunable dielectric materials for frequency agile microwave circuit applications.

This is due to an increased demand for wireless communication systems that offer high speed data rates, flexibility, multiband operation, adaptability, low power consumption, small size and low cost.

Nowadays different methods are employed to synthesize BST for different applications with different morphology and properties. Each method has its own merits and demerits. Among other nano materials $Ba_{1-x}Sr_xTiO_3$ has attracted attention due to i) high chemical stability ii) high permittivity iii) high tunability iv) low dielectric losses at room temperature. Properties of nano particles differ from bulk due to large surface to volume ratio and small size. Various methods of synthesis are i) solid state reaction ii) sol-gel method iii) hydrothermal methods iv) spray pyrolysis v) combustion synthesis vi) chemical co-precipitation vii) pulsed laser deposition viii) RF sputtering ix) CVD x) electrostatic spray assisted vapor deposition. Sol gel method is time consuming, costly and its starting materials are sensitive to moisture, temperature and light. The combustion synthesis technique is very important from point of view of preparation of very high purity nano materials. The advantages of the combustion route over other above mentioned techniques is that it is economical, produces uniform sized particles, energy efficient, less contamination and high production rate.

Factors that determine the properties of BST are grain size, sintering temperature, and grain morphology, sintering conditions, doping amount, structural defects and porosity. The powder property depends on the process parameters which are governed by the kinetics of the combustion reaction. For example addition of NH_4NO_3 enhances the productivity of the powders. Also the fuel used in the combustion process has a significant effect on the properties of the powder. Though combustion is mostly carried out in the presence of citric acid but other fuels like glycine, ethylene glycol, urea,

tartaric acid etc. are also used. Since citric acid does not provide chelating action, EDTA which is a chelating agent is used in combination with the fuel.

Chapter 2

LITERATURE REVIEW

[2.1] LITERATURE REVIEW

Lazarevic et al. [1] prepared barium strontium titanate from polymeric precursors through pechini process (soft chemistry) which was carried our as three stage process from organometallic complex. The polymeric precursors used were Titanium (IV) isopropoxide, barium carbonate, strontium carbonate, ethylene glycol and citric acid. The main objective of this study is to find experimental conditions, so that the polymeric precursor method is applicable to BST powder synthesis without any formation of carbonates. In order to avoid the formation of carbonates, the organic material must be decomposed at low temperatures over a long time. BST powder was obtained after calcination at 800□C for 8 h and characterized by XRD, IR, BET, and SEM analysis. The obtained powder is highly agglomerated and exhibits grains size in micrometer range.

B. Wodecka-Dus et al [2] prepared sol- gel derived powders of the chemical composition $Ba_{0.6}$ $Sr_{0.4}$ TiO_3 (BST) in the preparation of ceramic samples. Barium acetate, strontium acetate and tetra butyl titanate were used as starting materials. The free sintered method was used for the final densification of ceramics. The ceramic samples were characterized in terms of their crystalline structure(X- ray diffraction), microstructure (SEM); chemical composition (energy dispersive spectroscopy), and dielectric properties. It was found that excellent crystalline ceramic samples exhibiting regular symmetry were obtained after sintering at 1450□for 4 hours. Temperature dependence of permittivity was studied in the temperature range of ferroelectric-paraelectric phase transition. It was found that the temperature of the electric permittivity maximum value T fits well with the Ba/Sr ion ratio. Chen feng kaO and wein –Duo Yang et al [3] prepared barium strontium titanate powder from citrate precursor.

Titanyl precipitate when added to barium strontium citrate solution reacted to form gel. The gel was dried to form powders of (Ba, Sr) TiO_3. At 500°C the gel decomposes to (Ba, Sr) carbonate and TiO_2. At 600°C (Ba, Sr) TiO_3 powder formation took place. pH range of 5-6 was maintained. 0.1 mole % of the free cations remained in the solution. Drying was done by 3 methods. 1) Freeze drying 2) vacuum drying 3) air drying. The powder obtained by freeze drying had the lowest degree of agglomeration and such powder when calcined at 1100°C were compacted and sintered at 1300 °C to obtain dense ceramic bodies with 95% theoretical densities. The chemical composition of $Ba_{0.5}$ $Sr_{0.5}$ TiO_3 citrate powder were analyzed chemically. Cation-anion ratios nearest to pH 5-6 range as per stoichiometry. At low pH deviation of Sr^{2+} is the greatest and a higher pH of 7-8, the deviation of Ba^{2+} is the greatest. Calcination at 1000°C for 8 hours. Bulk density increased with increasing sintering temperature. Highest density reached at 1300°C.

T. Mazon et al [4] prepared barium strontium titanate nano-crystalline thin films by soft chemical methods. Ferroelectrics have been extensively used in thin film forms, mainly for application as multilayer ceramic capacitors (MLCCs) and dynamic random access memory (DRAM). BST is most extensively investigated for its high dielectric constant, low dielectric losses and good thermal stability. Electrical properties of BST is closely linked to its microstructural feature and fabrication process. The temperature of heat treatment for preparation by chemical methods, if high improves the crystallinity and electrical properties but the process becomes very inconvenient and grain size control is difficult. $Ba_{0.65}$ $Sr_{0.35}$ TiO_3 nano-crystalline thin films, which were produced by soft chemical methods were crystallized at low temperature using microwave oven. The films obtained were crack free, well adhered and fully crystallized. The nano grain size was observed. High dielectric constants up to 800 reach at 100 KHz. The charge

storage densities are suitable for use in 64 Mb and 265 Mb DRAMs. Dissipitation factor was 0.01 at 100 KHz. Here carbonates of Ba, Sr are used as raw materials.

M.Enhenssari et al [5], proposed synthesis and characterization of barium strontium titanate (BST) micro/nanostructures prepared by improved methods. Nowadays different methods are employed to synthesize BST for different applications with different morphology and properties. Wet chemical methods for preparation of BST nano particles are conducted at low temperature and yet offers good compositional and structural control of the product. Processing temperature is 60□C with precursor materials $Ba(OH)_2.8H_2O$, $Sr(OH)_2.8H_2O$, $Ti(OB_4)_4$ and deionized water. Post synthesis annealing has a strong influence on the lattice symmetry of nano particles. Hydrogen is present in the interstitial site due to aqueous solution. Observations from SEM, TEM, XRD, indicated particles were crystallized. Chemically stoichiometric and 50nm in diameter. BST nano particles prepared by this process are very useful for making high quality ceramics and composites.

Another improved method was the composition and shape control of BST nano crystals via solvothermal route. Mixture of ethylene diamine and ethanolamine as the solvent have been synthesized by the solvothermal method using barium acetate, strontium nitrate and tetrabutyl titanate as precursors. 5 samples with decreasing Ba/Sr ratio were prepared. Improved crystallinity with increasing strontium content. Particle morphology changes from irregular to polygon to cubic as Sr content increases. The increase in particle size with the increase in Sr proportion in BST samples is probably due to different growth rate with different Sr proportions in the product, because the solvent molecules have a stronger binding force to barium than

to strontium. Nano particles are crystalline without defects, such as dislocation, further confirming the nano crystalline nature of the solvothermal synthesized BST.

Ala'eddin A.saif et al [6] did research work on AFM study of multilayer sol gel $Ba_xSr_{1-x}TiO_3$ thin films. Surface morphology plays an important role in the understanding of thin films. Studies focused on the surface roughness of BST thin films show that the grain size and surface roughness increases with the increasing annealing temperature. In this work BST thin films are prepared with different Ba/Sr ratio and different film thickness are prepared by the sol gel technique and surface roughness and grain size are determined using Atomic Force Microscope. Barium acetate, strontium acetate and titanium isopropoxide were used as starting materials. Glacial acetic acid and 2-methoxy ethanol as solvents. Three different solutions with Ba/Sr ratio of 50/50, 70/30 and 80/20 were prepared and labelled as BST50, BST70 and BST80. BST thin films were spin coated layer by layer on SiO_2/Si substrate with a heating procedure. For each layer BST thin film was baked at 200□C for 20 min to vaporize organic solvents. Then heated at 500□C for 30 min in an O_2 atmosphere. The process is repeated for 4 layers. Finally it was annealed at 800□C for 1 hour in an O_2 atmosphere. 1-5 layers for each composition samples were prepared. Film thickness was measured for each case. From the AFM analysis, the microstructure such as grain size, surface roughness is one of the key parameters determining the dielectric properties of the thin film.

The electrical properties of the BST thin films are closely linked to the microstructure of the film such as grain size, cracks, pin holes and roughness. The root mean square (RMS) roughness increases with the thickness as well as with the increasing Ba content. Grain sizes increase with the increasing Ba content and film thickness. The

results show that the sol gel technique has high efficiency in fabricating high quality BST thin films on SiO_2/Si substrate. Very dense, crack free films are formed with low surface roughness and possessing larger grain size. Increasing trend in surface roughness with increasing grain size.

[2.2] OBJECTIVE OF THE WORK

In the present work following tasks have been undertaken:

- Preparation of $TiO(NO_3)_2$ and hence following the combustion synthesis route for powder preparation of barium strontium titanate with chemical formula $Ba_{0.8}Sr_{0.2}TiO_3$.
- Maintaining the **metal : fuel : oxidant** ratio as 0.8:0.2:1.5:12:0.1
- Preparation of bulk pellet samples
- Sintering behavior and AP , BD measurement
- Determination of Microstructure and dielectric behavior of the bulk samples.
- Preparation of thin film coating on alumina substrate.
- Characterization of the alumina coated substrates.

Chapter 3

EXPERIMENTAL PROCEDURE

[3.1] PREPARATION OF TITANIUM OXY-NITRATE SOLUTION [$TiO(NO_3)_2$]

The precursors required the preparation of $TiO(NO_3)_2$ are TiO_2 powder, sulphuric acid (H_2SO_4), and ammonium sulphate $(NH_4)_2SO_4$. They are taken in the amounts 5gm,120ml and 40 gm respectively. TiO_2 can only be dissolved in H_2SO_4 and forms $TiO(SO_4)$. And $(NH_4)_2SO_4$ enhances the rate of formation of $TiO(SO_4)$. The reaction kinetics increasing on increasing the temperature to 90-95°C.

Firstly, $(NH_4)_2SO_4$ was added to concentrated H_2SO_4 and continuously stirred till it dissolves completely. Then 5gms of TiO_2 was added to the above solution and vigorously stirred so that the suspension turns into a clear solution while on a hot plate. The reaction is given as:

$$TiO_2 + H_2SO_4 \longrightarrow TiO(SO_4) + H_2O$$

After the solution was cooled for a long time for about a day, it was diluted with distilled water upto 1.5 L. The solution was divided in 2 beakers and titrated against NH_4OH (ammonia solution) till white precipitate was completely formed.

$$TiO(SO_4) + 2\ NH_4OH \longrightarrow TiO(OH)_2 + (NH_4)_2SO_4$$

The precipitate was formed due to the formation of $TiO(OH)_2$ and $(NH_4)_2SO_4$ was suspended in the solution. Here the addition of NH_4OH solution was carried out until the pH turns 7. Precipitate settles down leaving SO_4^{2-} ions at the top. The precipitate is washed with distilled water again till it becomes sulphate free. The precipitate free from sulphate ions was filtered using Buckner funnel (arrangement used for filtration). The precipitate dries out in a period of 2-3 days. An ice bath was required and the beaker with 300 ml of distilled water and 300ml of HNO_3 in 1:1 ratio were taken and the precipitate was dissolved with continuous stirring. So a clear solution of $TiO(NO_3)_2$ is prepared by the above detailed procedure.

[3.2] ESTIMATION OF PREPARED $TiO(NO_3)_2$

5 ml of $TiO(NO_3)_2$ solution was taken in 2 beakers.

In each beaker NH_4OH solution was added so as to precipitate it.

2 separate arrangements were made with Watman 42 filter paper to filter the above precipitate. The residue is taken in 2 separate crucibles and fired at 900□C for 2 hours.

In 5 ml, 0.0296 gm. of TiO_2 was found.

So 1000 ml will contain 5.92 gm of TiO_2.

Molecular weight of TiO_2 = 79.82

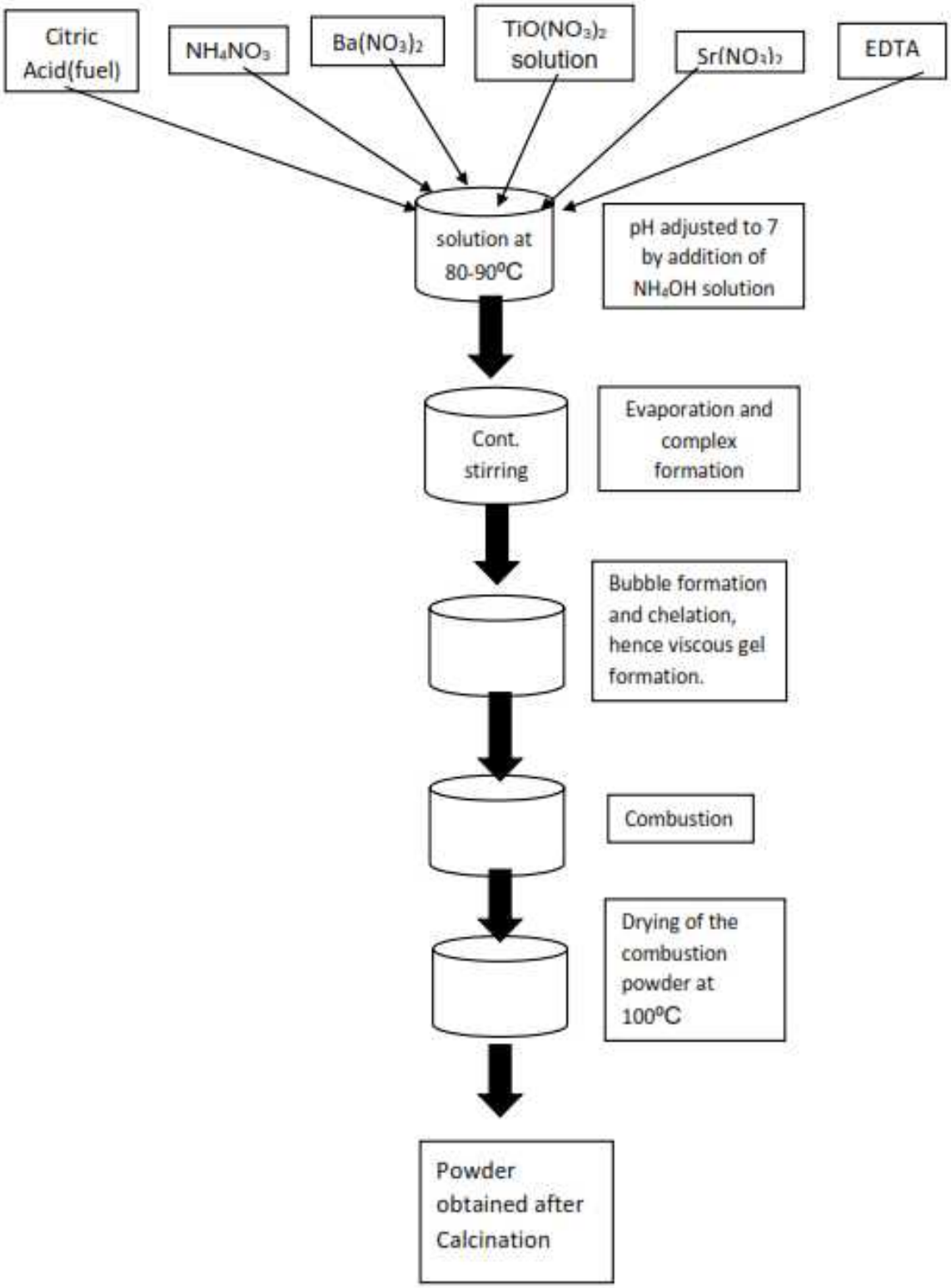
So strength /molarity of the $TiO(NO_3)_2$ solution is 0.0741 M

[3.3] PROCEDURE FOR COMBUSTION SYNTHESIS

Combustion synthesis technique was used for the preparation for BST powder with formula $Ba_{0.8}Sr_{0.2}TiO_3$. Here the metal ion to fuel to oxidant ratio to be maintained is 0.8:0.2:1.5:12:0.1. The metal ions are of barium and strontium, fuel is citric acid and ammonium nitrate is the oxidant and EDTA is the chelating agent. Combustion synthesis is a relatively new technique for synthesizing of phase pure powders. It is the reaction between metal complexes formed with the help of chelating agent, fuel and the oxidant. The precursor materials are the nitrates of Barium and strontium. NH_4NO_3 is a combustion promoter and enhances the productivity of combustion powder.

After weighing of calculated amounts of the precursor materials based on the mentioned ratio, they were taken in a beaker containing 200 ml $TiO(NO_3)_2$ and placed on a hot plate with temperature of 80-90□C. NH_4OH solution was added till the pH turns 7. This involves evolution of huge amount volatile matter. The solution slowly turns viscous. After a period of time the viscous solution turns into a gel and changes to brownish black in color. The gel undergoes dehydration to form a fluffy mass that rises to the mouth of the beaker and self-ignites with huge amount of gases being liberated. Hence a brownish black powder or better known as combustion ash is allowed for drying overnight as it is hygroscopic in nature. All the powder from the beaker is retrieved for calcination. Calcination temperature is decided by the DSC/TG results.

[3.4] FLOW CHART OF BST POWDER PREPARATION



[3.5] POWDER CHARACTERIZATION

[3.5.1] Thermal Decomposition Behavior of the Gel:

A part of the gel during the synthesis procedure is taken for DSC/TG characterization. Thermal decomposition nature of the gel has been studied using Netzsch, STA 449C. The DSC/TG patterns were plotted as a function of temperature and time up to 1000□C. The heating rate was 5□C/min. Alpha alumina was used as the reference material

[3.5.2] Preparation of bulk sample:

The calcined powder which was now off white in color was grinded in the agate mortar by saturating it in isopropyl alcohol. This was done so that there was no loss of the material and also helps in uniform grinding of the powder. The powder after grinding was dried for a period of half an hour under the IR lamp. The calcined powder was then mixed with 4 to 5 drops of PVA (poly vinyl alcohol) binder. The mixing of the binder was also carried out in the agate mortar for uniform mixing. The binder mixed powder was also dried and powder was pressed at 4 US ton in 12.5 mm diameter dies in the hydraulic press (10T, carver industries, USA). The holding time was given as 90 seconds for each sample. In the later part sintering schedule was decided. Sintering of the pressed green samples was done in the temperature range 1250□C–1300□C with intermediate binder burn out temperature of 600□C. Holding time in the electrical furnace was 1 hour at 600□C and 4 hours at the preferred high temperature. These sintered samples were used for further characterization and analysis.

[3.6] Preparation of alumina substrates for coating:

Commercial alumina substrates (0.1mm thickness, 99% Al_2O_3) were used for depositing thin film. 12 pieces of the alumina substrates of the dimension 2X2 cm. were cleaned by ultra-sonication. The above procedure was carried out by dipping of substrates in acetone and kept for ultra-sonication for 3 minutes. After the completion of 1 round, the sides of the substrates were reversed and again cleaned for 3 minutes. This ultra-sonication was carried out for the removal of unwanted contaminating particles from the surface of the substrates.

[3.7] Preparation of thin film on alumina substrate by applying viscous Sol:

Preparation of the sol was done in a similar manner as for preparation of powder for bulk BST. Here also 200 ml of $TiO(NO_3)_2$ was required. The other precursors, $Ba(NO_3)_2$, $Sr(NO_3)_2$, citric acid, NH_4NO_3 and EDTA are also same as in case of bulk preparation. NH_4OH was added for pH balance. Sol prepared is in the stoichiometric composition of $Ba_{0.8}Sr_{0.2}TiO_3$. The Sol preparation was done at low temperature 60-80□C with slow stirring. The only difference in this technique from the combustion synthesis is that the heating was stopped as soon as the bubbles start appearing.

Due to its simple procedure Dip Coating method was adopted. In this method the alumina substrate is dipped in the Sol prepared and dried each time. 3 Alumina substrates with 15, 20 and 25 coatings were prepared. After each coating the sample was dried under the IR lamp. The drying by microwave oven is not recommended because there is high and rapid thermal energy transfer of the coated film which leads to uncontrolled combustion. Hence this method was discarded. The dip coated samples were annealed at 800□C and were used for XRD analysis.

Sample 1d	15 coatings
Sample 2 d	20 coatings
Sample 3 d	25 coatings

Table 1 – thin film samples with number of coatings

[3.8] Preparation of Thick Film Coating on Alumina substrate:

BST gel of the composition $Ba_{0.8}Sr_{0.2}TiO_3$ was prepared in 2 batches. The gel was dried at 100□C and subsequently calcined. The calcined powdered sample was grinded in the agate mortar with addition of isopropyl alcohol. The powder is ground till very fine particles are obtained. This powder after drying under the IR lamp is mixed with Ethylene Glycol which used as the plasticizer and PVA as the binder. 5 substrates with different number of coatings are prepared. Here the coating is done by painting the paste prepared on the alumina substrate surface with help of a paint brush. The plasticizer provides flowability to the paste.

Sample 1p	2 coats
Sample 2p	3 coats
Sample 3p	4 coats
Sample 4p	5 coats
Sample 5p	6 coats

Table 2- – thick film samples with number of coatings

[3.9] DENSIFICATION STUDY

Bulk density and apparent porosity measurements are made for the bulk samples by following the Archimedes principle. In the present study kerosene oil is used instead of water.

[3.10] MICROSTRUCTURE ANALYSIS:

Microstructure of sintered pellet and thick film coated samples has been studied using Scanning Electron Microscope (JOEL-JSM 6480LV). The generator voltage was 15kV. Since the samples are insulating in character, they are electroplated with platinum for making the surface conducting.

[3.11] PHASE ANALYSIS:

The samples of the calcined powder, sintered sample, and the thin film dip coated alumina substrate were analyzed for the phase present using X-ray diffraction (Philips PAN analytical, the Netherland) using CuK_{α} radiation. The current was 25mA and the generator voltage was 35KV. Philips X'pertHighscore software was used to analyze the phases present in the given samples.

[3.12] DIELECTRIC MEASUREMENT

The sintered pellet was polished with the help of emery paper. After polishing it was silver coated. This coated sample was cured for 1 hour at 600□C. Dielectric measurement of the sample is done at room temperature. The frequency range of 100Hz to 1 MHz was chosen for the dielectric measurement of the sample.

Chapter 4

RESULTS & DISCUSSION

[4.1] DSC Analysis

The Differential Scanning Calorimetry is a thermo-analytic technique. The material under study in this case BST gel and an inert reference usually alumina are made to undergo identical thermal cycles, while recording the endothermic and exothermic peaks. Thus the DSC data provides transformations that have occurred. Here the BST sample is subjected to the maximum temperature of 1000□C at 5□/min.

DSC curve below shows the endothermic (downward) and exothermic (upward) peaks. Hence the Calcination temperature is decided to be 800□C. Calcination of the gel samples after the combustion process is done at 800□C for 2 hours. In the calcination process the blackish brown gel is converted to off white color powder. A major drop at 800□C shows that crystal formation occurs from oxide of barium and titanium which takes heat energy from the source.

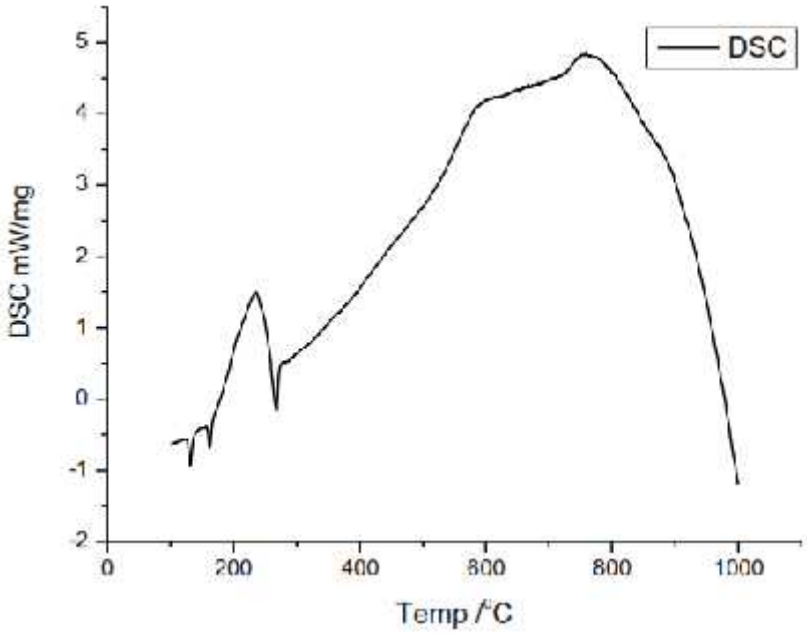


Figure 1 TG analysis of gel sample

[4.2] TG analysis

Thermogravimetric analysis measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are made for the BST samples to predict their thermal stability at temperatures upto 1000□C at 5□/min. the technique characterizes material based on the mass loss due to decomposition. In the following graph the decomposition pattern is given with major mass loss at 300□C and a nearly constant curve in the latter part of temperature change.

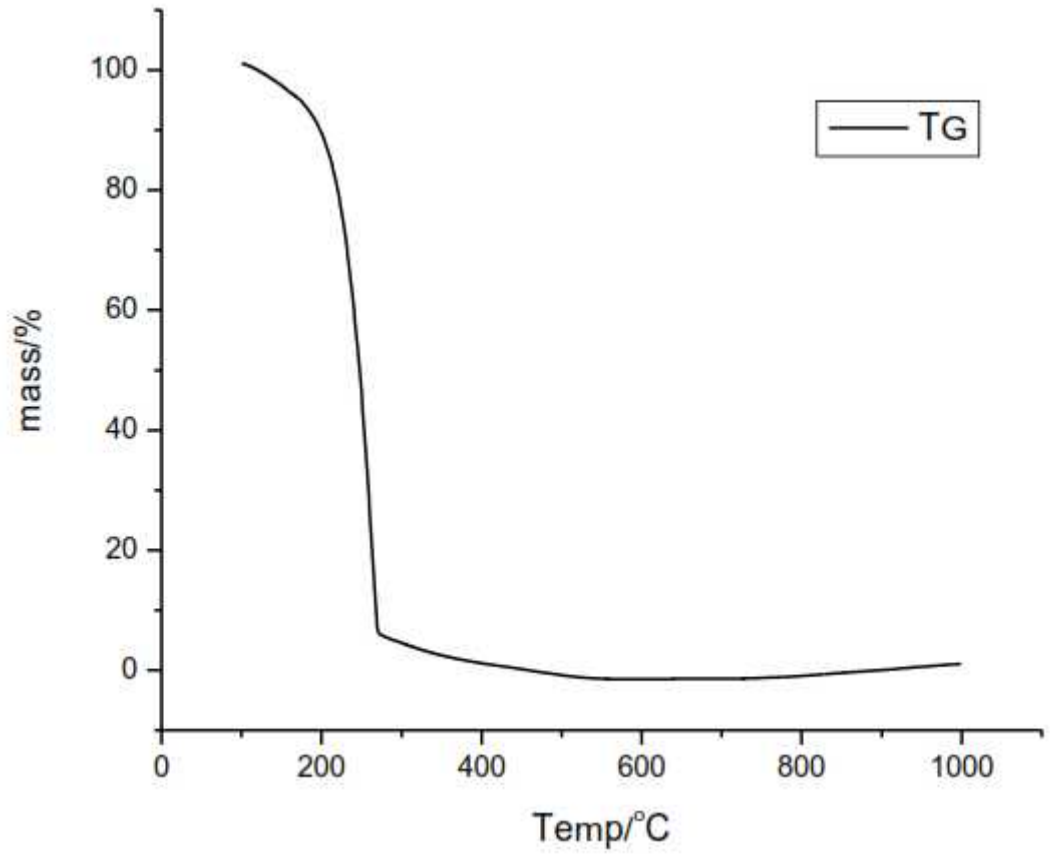


Figure 2 – TG analysis of gel sample

[4.3]Density Measurement

Batch 1 - After the preparation of the first batch of samples, they are pressed at 4 US ton with a dwell time of 90 seconds in the hydraulic press. 2 pellets are prepared and sintered as given below:

Sample 1C	1250□C for 4 hours
Sample 2C	1300□C for 3 hours

Table 3 – schedule for sintering of samples

For bulk density and apparent porosity measurement, dry weight of both samples is first taken. Then samples are dipped in kerosene oil with specific gravity 0.81g/cc for de-airing in the vacuum set up. Then suspended weight is taken by the Archimedes principle and soaked weight is taken by soaking the sample by a rag.

Sl. no	Dry weight (D)	Soaked weight (W)	Suspended weight (S)	Bulk density D/(W-S)	Apparent porosity (W-D)/(W-S)
Sample 1C	0.7423	0.8004	0.6315	3.56	27.86%
Sample 2C	0.7730	0.8738	0.6583	2.905	37.88%

Table 4- B.D and A.P measurement

Since the results were inconsistent with the literature another batch was prepared for the same. Here the main problem with pellets was that they had undergone bloating due to incomplete binder burnout. This was due to the fact intermediate temperature was not set. At intermediate temperature binder burnout takes place.

Batch 2 – BST powder with the same composition was again prepared. 2 pellets were made by pressing in the same way as above. Both the samples were kept at 600□C for 1 hour soaking time. This was the binder burn out stage. And then temperature was raised till 1250□C and soaking time 4 hours. Sintering is done Tube furnace.

After sintering, 1 of the 2 samples cracked and was of no further use. The 2nd pellet was taken for measurement in the above said manner.

SL no.	Dry weight(D)	Soaked weight(W)	Suspended weight (S)	Bulk density D/W-S	Apparent porosity (W-D/W-S)
Sample 3C	0.65	0.5476	0.6513	5.077	1.0154%

Table 5- B.D and A.P measurement

The results were well in consistent with the literature. Hence this sample is further characterized for XRD, SEM and dielectric measurement.

[4.4] XRD analysis

As X-ray diffraction analysis is a very effective characterization technique to get insight of crystalline phases present and the structure of basic crystalline structure (unit cell) in bulk, that was used successfully to determine phases of calcined powder and sintered sample. It is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system. Powder diffraction (XRD) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples.

[4.4.1] XRD of Calcined and Sintered sample

From the following graphs the XRD results of the calcined and sintered samples were analyzed for the phase present using Cuk_{α} radiation. From the graphs it is confirmed that phase pure $Ba_{0.8}Sr_{0.2}TiO_3$ sample has been prepared by combustion synthesis and there are no impurity phases.

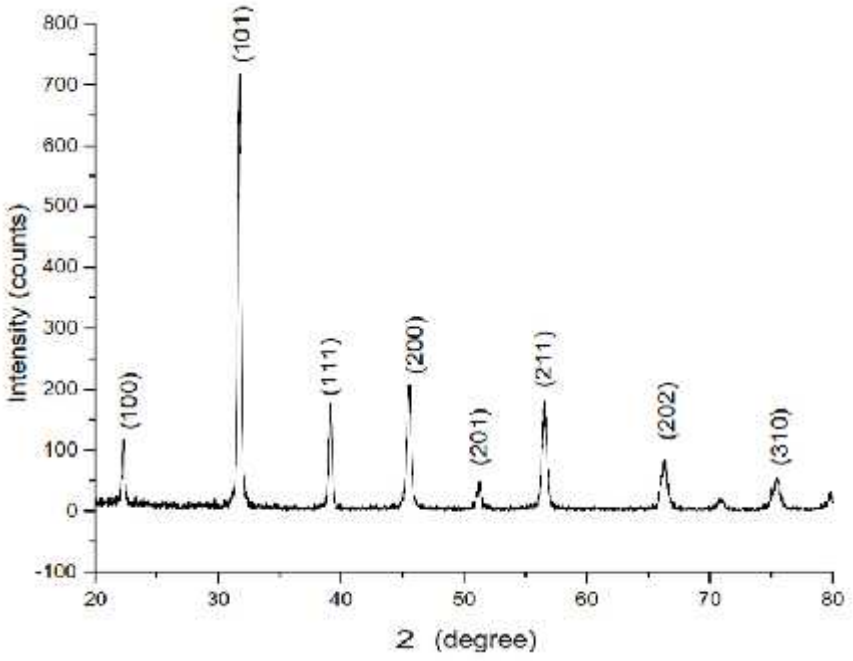


Figure 3- XRD of powder calcined at 800℃

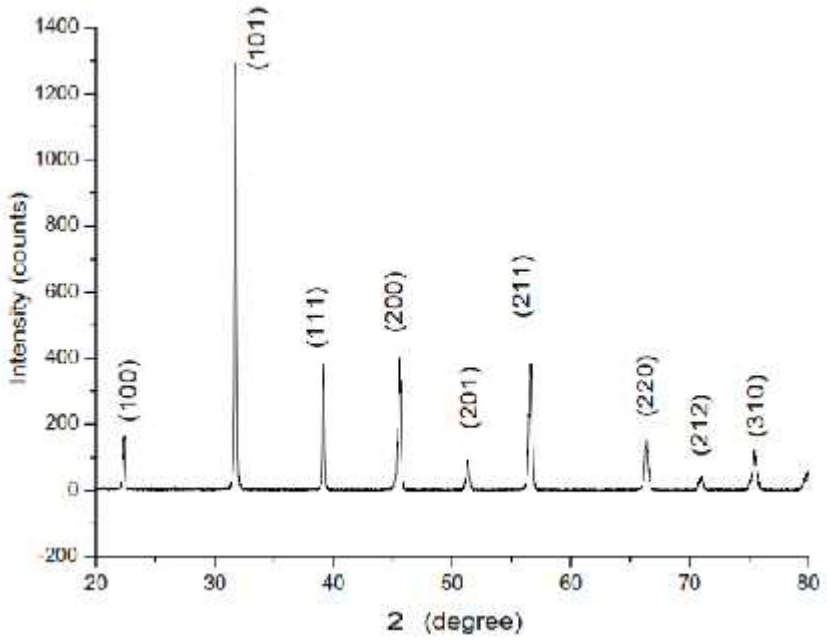


Figure 4 XRD of the pellet prepared sintered at 1250^{o}C for 4 hours.

The calcined powder being of the low temperature shows less crystallinity hence less sharp peaks. But due to sintering, densification and grain growth takes place and gives rise to higher crystallinity in the phase pure sample which is justified by the sharper peaks. High crystallinity confirms the formation perovskite structure. The peaks have been indexed based on the data from the XRD results and the lattice parameter is calculated from the d value of the highest peak which is equal to 2.81.

Lattice parameters were foundfrom the JCPDS file.

A = 3.9771 Å

B = 3.9771 Å

C = 3.9883 Å

From this it can be said that the crystal structure is tetragonal.

[4.4.2] XRD of thin film Samples

The XRD patterns of the Dip coated samples prepared by the sol gel technique are analyzed by comparing the XRD results of the pure alumina substrate and the dip coated alumina substrate. The dip coated sample with 25 number of coatings which was annealed at 800□C showed very faint peaks. From the graphs, very faint peaks of the $Ba_{0.8}Sr_{0.2}TiO_3$ were observed. The low intensity of the representatives of BST are attributed to using conventional powder diffraction modes. Glancing angle Diffraction technique could have given clear appearance of BST peaks on the alumina substrate. In this case the x-ray diffraction peaks of the alumina substrate subdues the BST peaks.

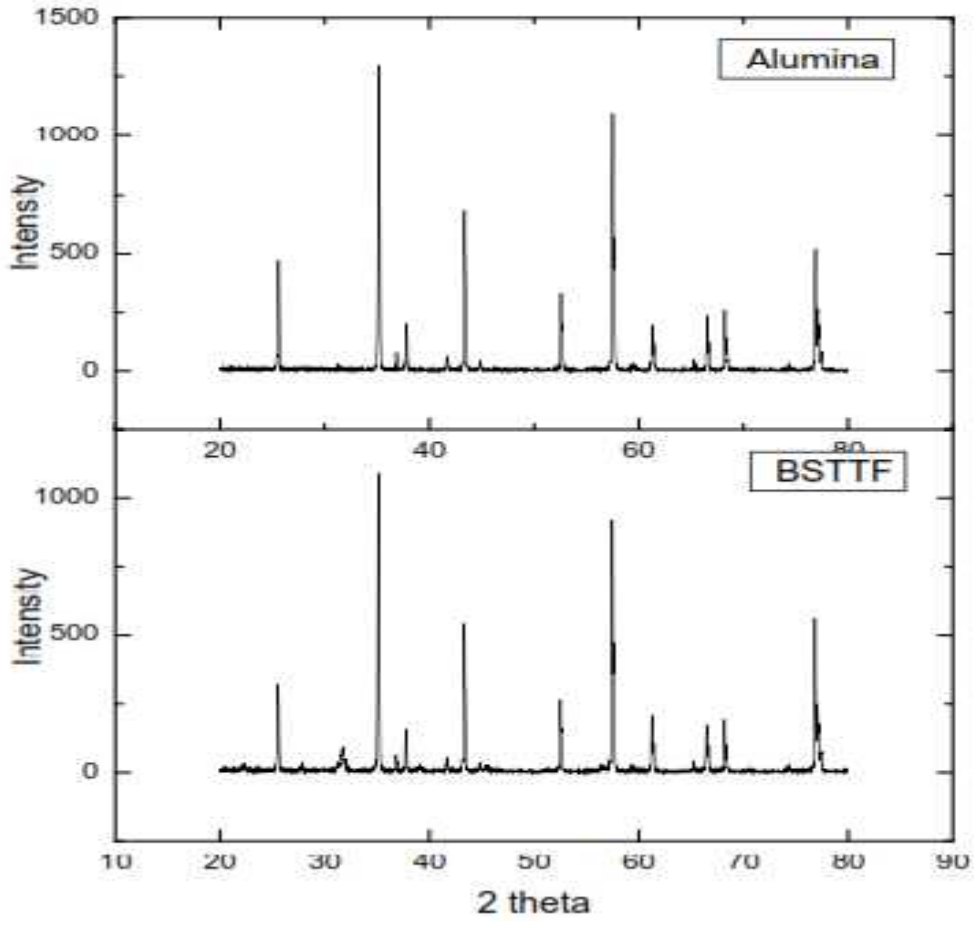


Figure 5 Comparison by XRD of thin film and alumina substrate

[4.5] SEM analysis

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern.

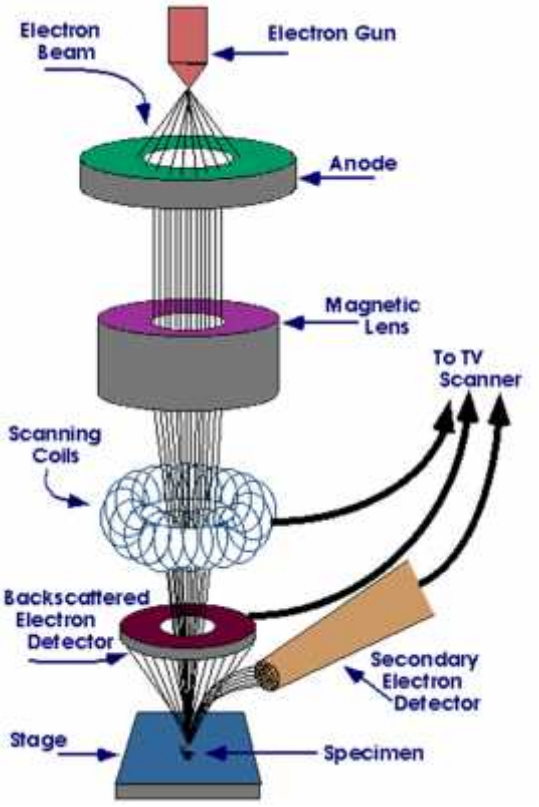


Figure 6 – schematic of SEM

A scanning electron microscope is a machine which comprises of an electron generating component called the electron gun, a column through which electron beam travels, a series of lenses that help to shape the electron beam, the sample chamber at the base, and a series of pumps to help keep the system under vacuum. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image.

[4.5.1] The BST bulk ceramic pellet was taken for SEM analysis. Here the microstructure of the sintered pellet is seen through. The sample was coated with platinum because they are insulating otherwise. Below are SEM pictures of the sample are mentioned.

Sample1-1

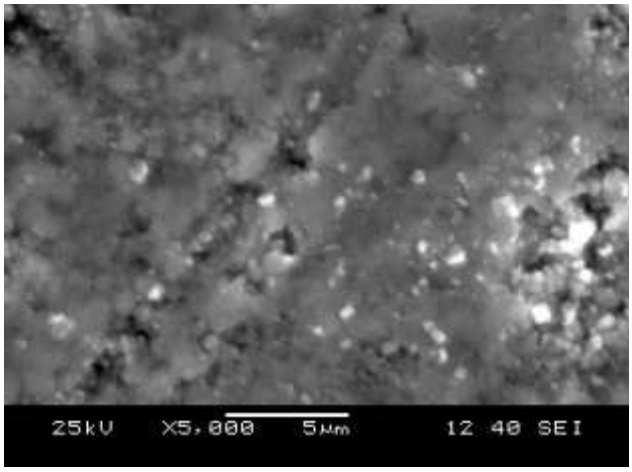


Figure 7(SEM of bulk)

Sample1-1

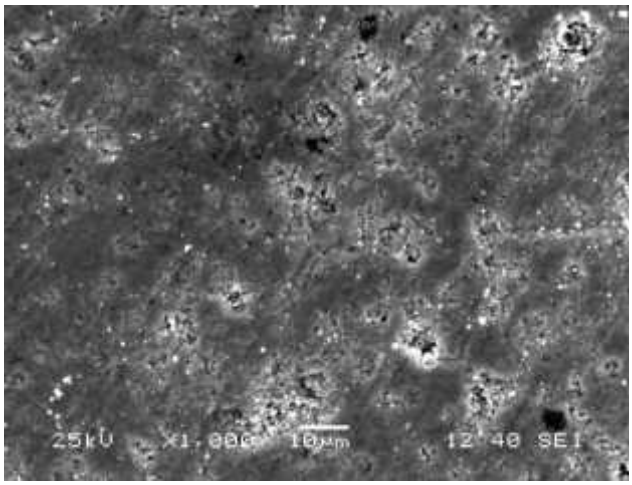


Figure 8(SEM of bulk)

The microstructure shows a compact nature and well distribution of grains. A few pored appear in the microstructure due to polishing of the sample on relatively coarse emery paper. As per observation the grain size lies between1-3 micron.

[4.5.2] Characterization of thick film

[A] Scanning electron microscopy of the BST coated alumina substrate thick films was performed .The samples were annealed before this .This thick film is formed by coating of 2 layers on the alumina substrate. The sample is p1.

Sample 4-1

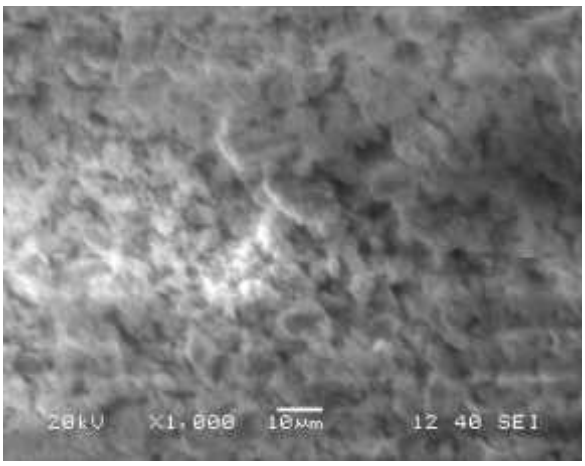


Figure 9 (SEM of thick film P1)

sample 4-2

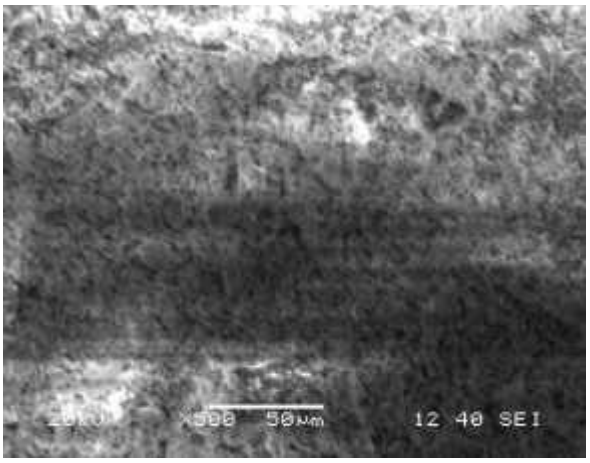


figure 10(SEM of thick film P5)

The surface is very rough and non-uniform. The SEM images at higher magnification shows horizontal lines of the brush marks.

[B] This sample P3 is coated 4 times with BST paste.

Sample 3-1

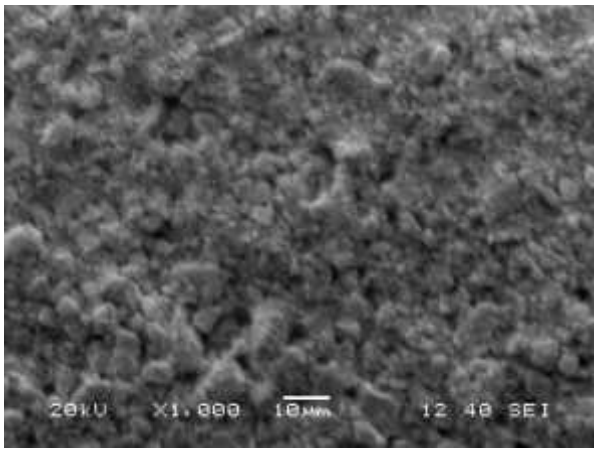


Figure 11(SEM of thick film P3)

sample 3-2

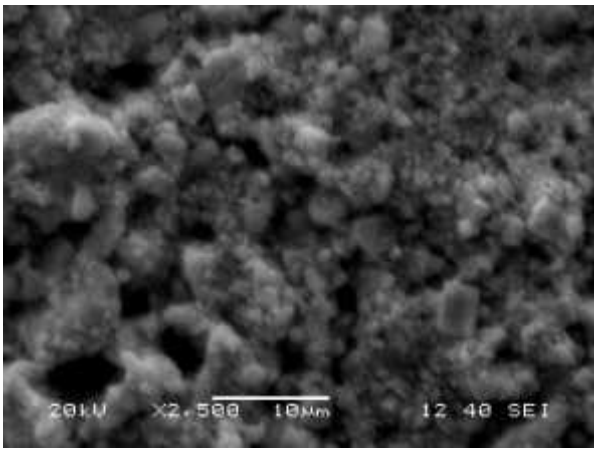


figure 12(SEM of thick film P3)

Sample 3-3

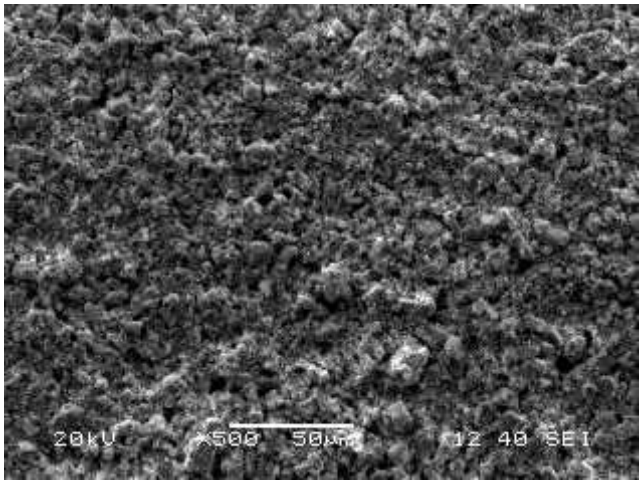


Figure 13(SEM of thick film P5)

This shows non-uniform layer formation. There is higher amount of porosity. The amount of agglomeration is quite high and the film is irregular. The larger particles are actually the cluster of smaller particles that have not yet undergone grain growth. Porosity is higher than in the 6 coated sample.

[C] This sample is coated with 2 layers. Sample name is P5.

.Sample 2 -1

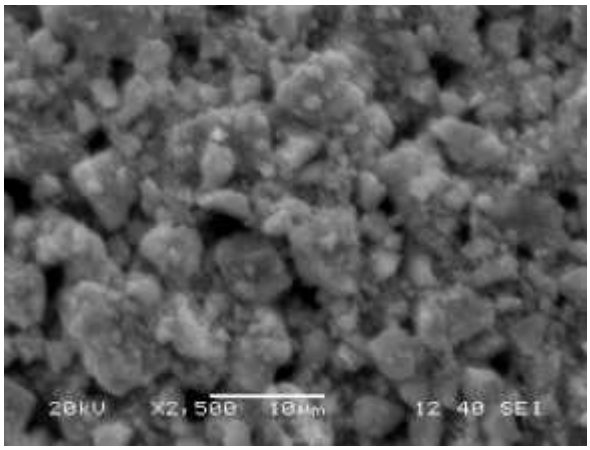


Figure 14 (SEM of thick film P5)

sample2-2

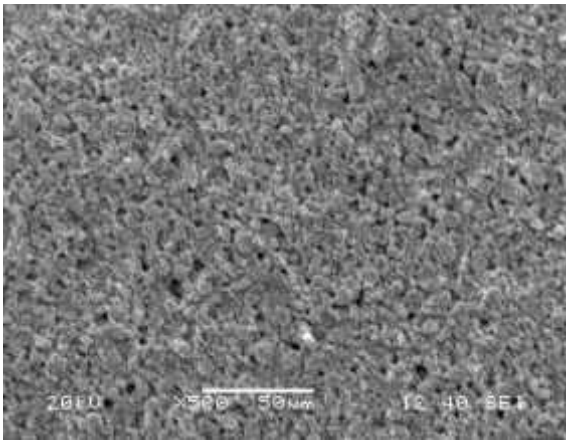


figure 15(SEM of thick film P5)

The particles are not in uniform size as appears in the image and higher magnification image shows significant porosity. Agglomeration to a little extent is also observed. This could be the result of making a paste using PVA. This sample is sample p5 that is it is coated for 6 times. At low magnification, grains can be seen as uniform, but the same grains look not so uniform at higher magnification. This sample has more homogeneity than the other coated samples.

[4.6] DIELECTRIC MEASUREMENT ANALYSIS

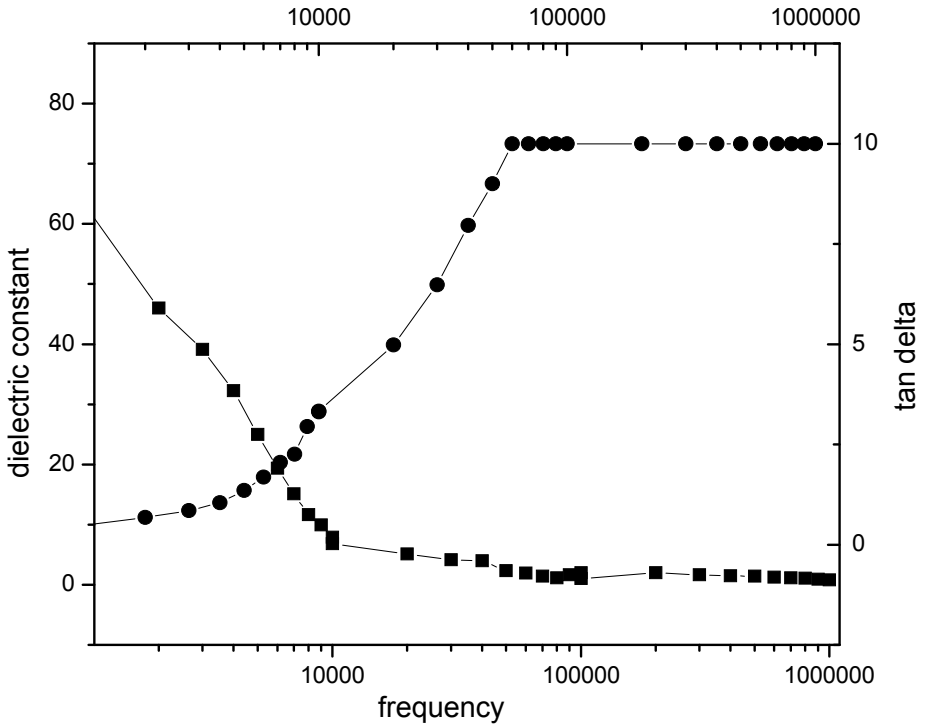


Figure 16 – dielectric constant and loss factor versus frequency

The Dielectric measurement is taken at room temperature. This is the plot of dielectric constant and tan delta versus frequency. The curve shows a fluctuating behavior with respect to the frequency. At higher frequency region (from several 100 kHz to MHz) the loss is found to be constant. The loss factor attains almost constant value if the domain wall motion is restricted and constant. In practice the relaxation time for charge transfer is depends on the applied frequency. Up to 10 kHz, the loss is found to be increasing. The decrease in permittivity up to the value of 10 kHz frequency is due to the interfacial polarization. Electroding effect is much more dominant at lower frequencies. The phenomenon is known as usual dielectric disper

Chapter 5

Conclusion & Further Scope of the Work

Conclusion and Further scope

BST ceramics were prepared successfully in the bulk form. The dielectric properties suggests that they could be used as capacitors in microwave devices. Thin film coating on alumina substrates was not significant. Same can be carried forward using i) relatively thick and viscous sol by changing the precursors or the starting materials ii) increasing the number of coatings iii) adopting a proper drying technique (furnace with airflow, Temperature 200-300□C). The thick film of BST was evident from the microstructure studies. Though some important electrical characterizations are needed, this work could be extended to develop tunable microwave devices.

Chapter 6

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